

Forensic Evaluation of Whitewash Fort Sumter National Monument

by

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Introduction

A thin specimen of whitewash was removed from a casemate arch at the Fort Sumter National Monument (FSNM) by Mr. Rick Dorrance of The National Park Service in late 2009. The specimen was taken from an area to the right of the sally port (1st casemate by the powder magazine) and from a place where the whitewash was peeling away from the brick faces. The purpose of this investigation was to characterize the whitewash and to recommend methods of preservation that might protect the historic fabric.

Methods

The specimen was examined using a scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDAX) capability. Because of the friable nature of the specimen, traditional petrographic methods were considered as impractical. The EDAX provided chemical analysis information on the specimen.

The mineralogical analysis was obtained using X-ray diffraction (XRD). Thermal analysis techniques were used to further characterize the specimens and confirm phase identifications by XRD.

Findings

The outer front or exposed surface of the whitewash is shown in a SEM photomicrograph (Figure 1). The phases present are “sand” (S), a cementitious matrix (M), and “large” pores (P). Smaller pores, also called “capillaries”, are in the matrix. To the naked eye, the exposed surface of the whitewash appeared as perfectly smooth.

The edge of the fragment reveals that the back surface has a very porous appearance in contrast to the front surface (Figure 2). The fine porosity implies that the material is highly susceptible to liquid and vapor permeation.



Figure 1: Outer Exposed Surface of the Whitewash Coating



Figure 2: Edge of Fragment (Exposed Surface to the Right and Back Surface to the Left)

The chemical analysis by EDAX of selected areas from the front surface is provided in Table 1. The following observations are made:

- The aggregate appears to be low purity dolomite rock used as sand size particles (See XRD data below).
- The magnesium oxide content of the matrix phase suggests use of fine dolomitic lime to obtain the desired white color.
- The matrix phase appears to be carbonated.
- Sulfur is present in the matrix phase.
- Chlorine is detected on all surfaces.

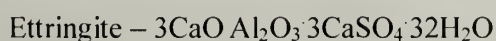
Table 1: Chemical Analysis of Whitewash by EDAX

Constituent	Overall Composition	Aggregate 1	Aggregate 2	Matrix 1	Matrix 2
SiO ₂	40.3	92.0	80.1	32.4	15.2
Fe ₂ O ₃	3.3	1.6	1.3	8.0	4.7
TiO ₂	1.0	0	0	0.5	0.1
MgO	16.7	3.1	5.6	20.4	13.8
CaO	20.5	3.7	7.0	28.6	11.1
Na ₂ O	1.0	0	0	0.9	1.0
K ₂ O	1.2	0	0.5	0.7	0.6
Cl	0.6	0.2	0.3	0.7	0.4
SO ₃	0	0	0	0.5	0.2
CO ₂	14.5	0	9.3	2.7	50.5
Sum	101.9	101.2	105.4	98.6	99.8

Note: The quantity “0” means below detection limits.

The X-ray diffraction analysis is presented in Figure 3, where the major phases identified are calcite (calcium carbonate) and dolomite. Since quartz was not identified, the aggregate in the whitewash appears to be a relatively high silica content dolomite. Dolomite was likely used because of its high “whiteness”.

The minor phases identified were the complex salts ettringite and thaumasite with formulas given as:



Both ettringite and thaumasite have been associated with failures of mortars and renders¹. The mechanism of failure involves crystal growth that creates pressure within the affected material - resulting in a weakening of the cementitious matrix and in the peeling of the renders². Böke and Akkurt found ettringite associated with failures of lime based repair material in historic structures where there was substantial moisture exposure³.

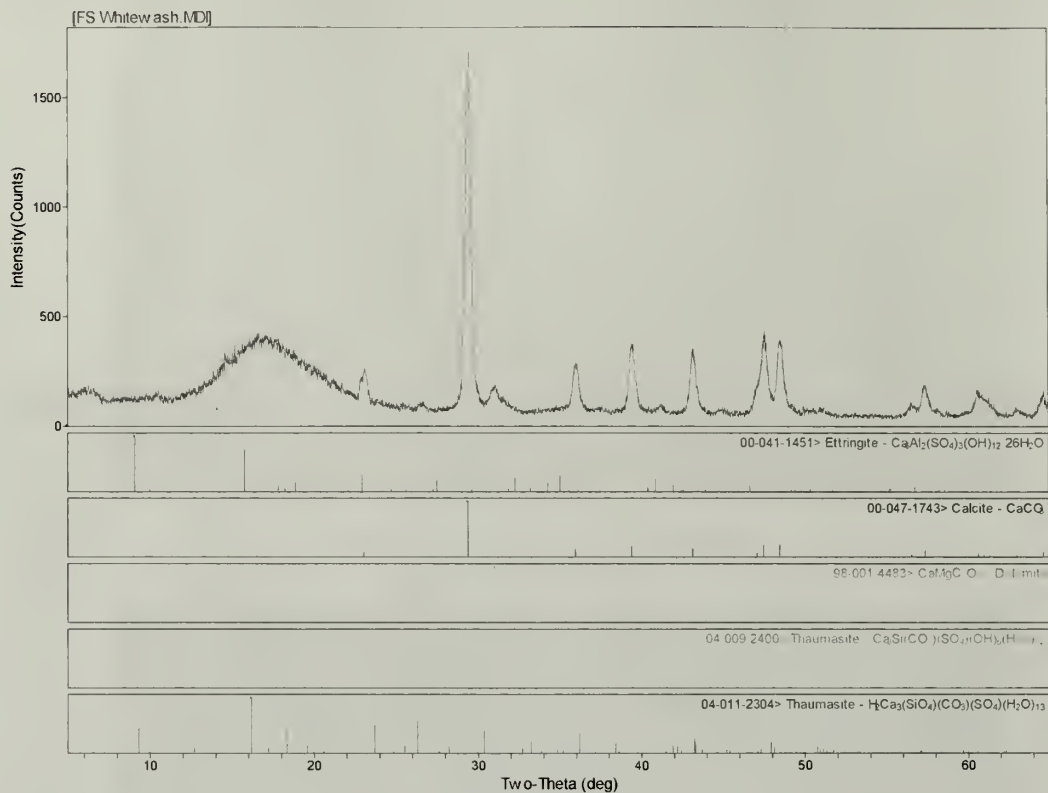


Figure 3: X-ray Diffraction Analysis of the Whitewash

¹ N. J. Crammond, Thaumasite in Failed Cement Mortars and Renders, *Cement and Concrete Research*, 15 (1985) 1039-1050.

² F. Venaile, M. Setti, C. Rodriguez-Navarro, S. Lodola, W. Palestra, and A. Busetto, Thaumasite as decay product of cement mortar in brick masonry of a church near Venice, *Cement and Concrete Composites*, 25 (2004) 1123-1129.

³ Hanson Böke and S. Akkurt, Ettringite formation in historic bath brick-lime plasters, *Cement and Concrete Research*, 33 (2003) 1457-1464.

The thermal analysis of the whitewash is given in Figure 4, where the following observations are made:

- The mass change below 400°C is reminiscent of natural cement dehydration; however, the weight loss and water evolutions are found to be due to the dehydration of ettringite and thaumasite, as discussed below.
- The “twin” CO₂ evolutions at about 650°C and 800°C are characteristic of dolomite and/or carbonated dolomitic lime.

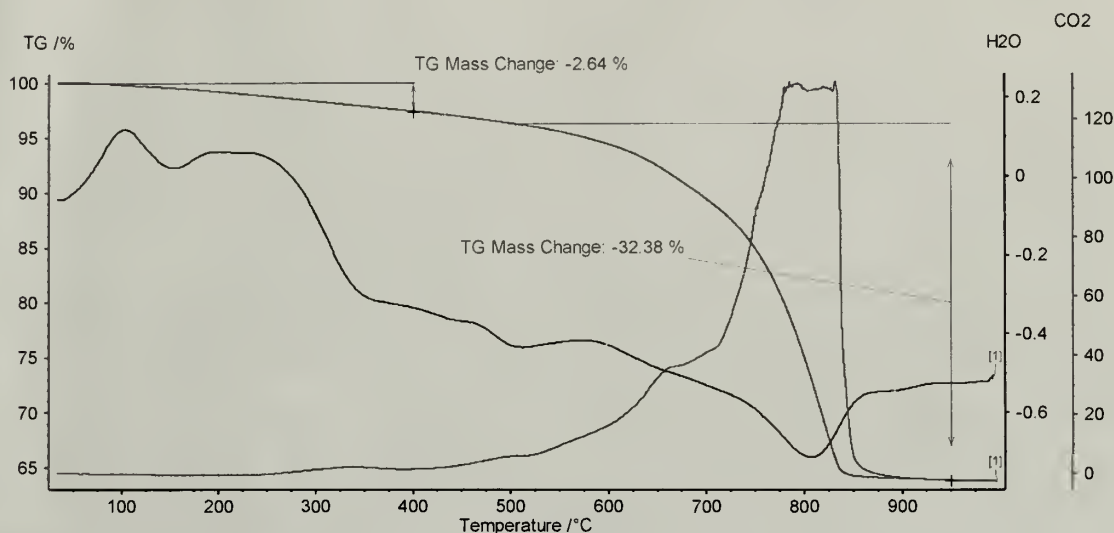


Figure 4: Thermal Analysis and Evolved Gas Analysis on Heating of Whitewash

Antao et. al. found ettringite to exhibit decompositions at 149°C and 753°C by thermal analysis⁴. Further, Drábik et. al. found that thaumasite exhibits extreme weight loss on heating in the interval 50-100°C⁵. Given the observations in Figure 4, there is general correlation with the weight loss and water vapor evolution in the whitewash to the results reported in the literature. Note, the differences in the heating rate between this study and those used in the literature resulted in minor shifts in the thermal responses.

⁴ S. Antao, M. Duane, and I. Hassan, DTA, TG, and XRD Studies of Sturmanite and Ettringite, *The Canadian Mineralogist*, 40 (2002) 1403-1409.

⁵ M. Drábik, D. Tunega, S. Balkovic, and V. Fajnor, Computer Simulations of Hydrogen Bonds for Better Understanding of the Data of Thermal Analysis of Thaumasite, *Journal of Thermal Analysis and Calorimetry*, 85 (2006) 469-475.

Brief Discussion and Conclusions

The peeling or scaling of whitewash at FSNM is caused by thaumasite and ettringite formation within the whitewash and on the underlying brickwork. Two conditions are necessary for the formation of these destructive phases:

1. These must be an environmental source of sulfur, and this author found significant content of sulfur salts on the surface of the brick masonry at FSNM⁶.
2. There must be substantial moisture present⁷.

While the forensic analysis indicates reasonable certainty in the deterioration mechanism, the physical appearance of peeling/scaling as a consequence of thaumasite and ettringite formation is of practical importance. Corinaldesi et. al. provides photographic evidence of sporadic failures on masonry renders that is reminiscent of the situation with the whitewash at FSNM⁸.

For preservation of the whitewash, protection from moisture intrusion is the only sure method to retard decay. Some literature exists on the use of barrier coatings, but these are not considered as authentic to the historic fabric. It is not well demonstrated that barrier coatings are either aesthetically acceptable or effective treatment strategies. Further, materials based on Portland cement should be only used at FSNM with caution as they contribute sulfur to the masonry system.

⁶ D. Brosnan, Characterization and Forensic Studies of Construction Materials from Fort Sumter National Monument, January 11, 2010 (A Report for The National Park Service). In this work, ettringite crystals were identified in the areas of prior masonry pointing with Portland cement based mortars.

⁷ J. Bensted, Thaumasite – background and nature in deterioration of cements, mortars, and concretes, *Cement and Concrete Composites*, 21 (1999) 117-121.

⁸ V. Corinaldesi, G. Moriconi, and F. Tittarelli, Thaumasite: Evidence for incorrect intervention in masonry restoration, *Cement and Concrete Composites*, 25 (2003) 1157-1160.